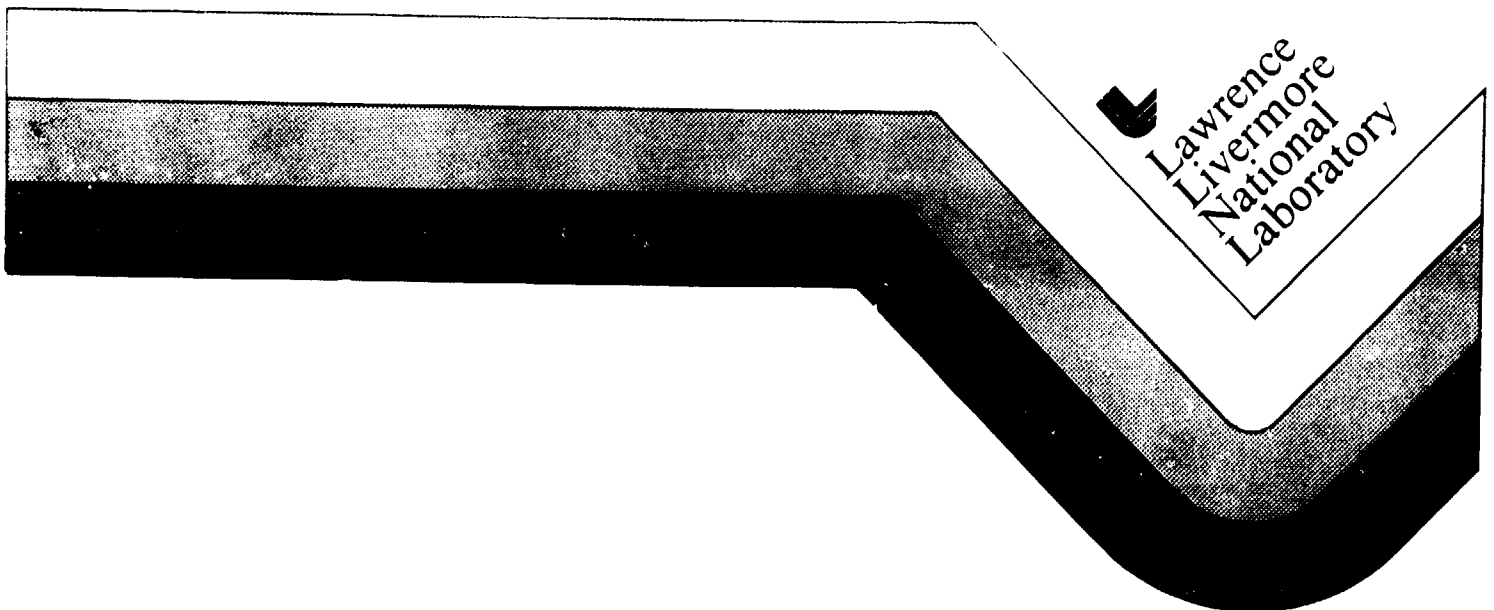γ

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DEVELOPMENT OF LOW DENSITY SILICA AEROGEL AS A CAPTURE MEDIUM FOR HYPER-VELOCITY PARTICLES

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SUMMARY OF FINDINGS AND ACHIEVEMENTS:

We have successfully made silica aerogel monoliths with bulk density as low as 0.025 gm/cc. We have observed a transition in the optical clarity from clear to cloudy, which occurs for densities between 0.03 and 0.04 gm/cc. We have established the effect of catalyst concentration on the density and clarity of silica aerogels. We clarify the problems associated with purity of the end product and the extraction process to achieve uncracked material.
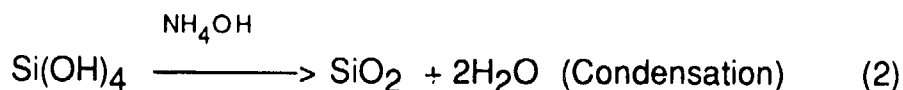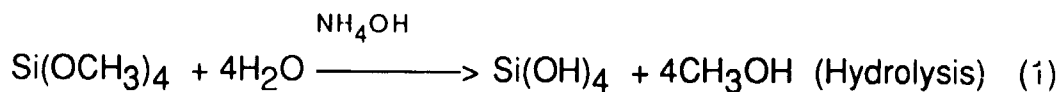
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I. OBJECTIVE AND APPROACH

The objective of this study is to develop micro-porous silica aerogel glass with optimal properties for its potential use as a capture medium of hyper-velocity particles. The important properties for this application are identified as ultra-low bulk density (i.e. < 0.1 gm/cc), high transparency to visible light, and purity (absence of organic and inorganic contaminants).

Our approach is to expand on our existing knowledge and experience concerning sol-gel chemistry and the extraction technology which we now use to routinely produce clear silica aerogel monoliths at densities higher than 0.1 gm/cc. We expect to push the existing technology toward ultra-low density aerogels and identify any limitations impeding the development of this material with optimal properties for the particle capture application.

II. ULTRA-LOW DENSITY AEROGELS

Silica aerogels are routinely formed and extracted to bulk densities as low as 0.1 gm/cc. The process involves the formation of a silica gel from the following reactions using a basic catalyst (NH_4OH):

$$Si(OCH_3)_4 + 4H_2O \xrightarrow{NH_4OH} Si(OH)_4 + 4CH_3OH \quad \text{(Hydrolysis)} \quad (1)$$

$$Si(OH)_4 \xrightarrow{NH_4OH} SiO_2 + 2H_2O \quad \text{(Condensation)} \quad (2)$$

The first of these reactions, the hydrolysis of tetramethoxysilane (TMOS) by water, is slow with base catalyst, relative to the condensation reactions. The overall rate to form the sol and then gel, is determined mainly by the hydrolysis. Spheroidal macroparticles grow from the condensed silica and link to form a continuously porous skeletal microstructure, surrounded by the alcohol solvent. Typical particle diameters range from 3 to 8 nm, and pore diameters range from 30 to 100 nm, depending on the density. The solvent is

subsequently removed from the wet gel by supercritical extraction in a high temperature autoclave, to prevent collapse of the delicate structure by strong capillary forces from the liquid. The remaining air-filled solid is called an 'aerogel'.

The approximate bulk density of the final aerogel is determined from the ratio of the weight of the silica to the volume of methanol that is generated from the reaction (e.g. 4 moles of methanol for each mole of silica). From the stoichiometry of the reactions 1 and 2, the expected bulk density of the silica aerogel would be about 0.27 gm/cc. In practice, reduced densities are achieved by adding methanol as a diluent in the initial solution mixture. While this results in lower density aerogels, the hydrolysis rate and overall time to gelation slows considerably. For example, using the dilution method, nearly 14 days are required to gel a solution targeted for an aerogel density of 0.04 gm/cc.

We have developed an alternative method that speeds the gel time for ultra-low density silica aerogels. We control the above reactions by using a sub-stoichiometric amount of water in reaction 1 to slow the hydrolysis somewhat, while refluxing to remove the reaction generated methanol. This method concentrates the remaining solution and condensation proceeds to form a sol with ultra-fine particles of silica. The sol is stabilized against gelation during and after the refluxing by adding a non-alcohol solvent, then it can be stored for later use.

The pre-condensed silica sol is then used to make gels of selected densities by simply diluting it with alcohol and using a base catalyst. The time to gelation is only a few days for the lowest densities, because the starting solution is already fully hydrolysed and partially condensed. We call this method the 'condensed silica' (CS) method. We have used it successfully to make silica aerogels having densities ranging from about 0.02 gm/cc to 0.1 gm/cc.

III. OPTICAL CLARITY OF AEROGEL

Even with its high porosity (>90%), the silica aerogel is relatively transparent because its microstructure consists of particles much smaller than visible wavelengths. In fact, Rayleigh scattering within the aerogel results in a distinctive bluish tint when viewing light scattered from it. The aerogel has a yellow color when viewing

transmission of white light through it. This is due to its higher absorption of ultraviolet wavelengths compared to the longer, visible wavelengths. This is seen in Fig. 1 which shows the absorbance of a typical 'clear' aerogel, over the wavelength range from 200 to 800 nm.

The clarity of silica aerogel stays qualitatively 'good' as the density is decreased from 0.1 gm/cc until an abrupt change in the clarity occurs for densities between 0.03 gm/cc and 0.04 gm/cc. This is shown in Fig. 2 where the clearer sample has a measured density of 0.043 gm/cc and the other sample has a density of 0.034 gm/cc. The difference in transmittance for the two samples is shown in Fig. 3. The reason for this transition in clarity is uncertain. We estimate that the dimension of the scatterers would be greater than 150 nm in order to produce the white coloration seen in the ultra-low density aerogels. However, examination of the microstructure of these aerogels using transmisson electron microscopy (TEM) (Fig. 4) reveals that the average particle sizes are less than 100 nm for both densities. To date, it has not been possible to obtain a meaningful pore size for this material by techniques such as TEM, SEM, porosimetry, or nitrogen adsorption, so we are unable to verify that pores as large as 150 nm exist in the aerogels. We believe, however, that as the density decreases, longitudinal pore dimensions may increase dramatically without a similar change in the transverse dimensions. If this happens, it would account for the increased scattering, but it would be difficult to detect. We continue to study this effect and hope to apply a recently developed replication method[1] with TEM imaging of the silica aerogel surface, to attempt direct measurement of the pore sizes in the ultra-low density aerogels.

IV. CATALYST EFFECT

The reaction rates for both the hydrolysis and condensation steps, and the microstructure of the gel, are known to depend strongly on the pH of the solution through the influence of the catalyst.[2] Also, the catalyst concentration affects the size of the primary silica particles, the degree of crosslinking between them, and subsequently, the strength of the microstructure.[3]

We have found that the overall shrinkage from the wet gel to the dried aerogel, is directly related to the catalyst concentration. Thus,

the final bulk density of the aerogel can be determined, with reasonable accuracy, using only two variables; the moles of TMOS and catalyst. We derived an empirical relation to predict the final density from these two variables, under conditions in which the water is a constant ratio with the TMOS and the batch volume is constant. The relation is:

$$D^{1/2} = 3.240 + 42.226\,T - 1.882\,C\,T + 0.036\,C^2 \qquad (3)$$

where D is the aerogel bulk density in gms/cc, T is the number of moles of TMOS, and C is the number of micromoles of NH_4OH. This relation holds well for densities between 0.02 gm/cc and 0.5 gm/cc, when $T > 0.03$ and $C < 10.5$.

The catalyst concentration also affects the clarity of the aerogel probably through its influence on particle size and the degree of crosslinking which affects the pore sizes. Differences in aerogel clarity can be seen in Fig. 5 which shows aerogel samples made from variations in T and C from the relation 3 above. In Fig. 6, the transmittance (percent of input light at 632.8 nm, transmitted per centimeter path length) is plotted for a range of aerogel densities, as a function of catalyst concentration used to make them. This plot shows that clarity can be improved with a higher concentration of base catalyst and that a sharp transition to opaque aerogels occurs for low catalyst concentrations. Note, however, that the catalyst concentration alone does not lead to the similar transition at ultra-low density, discussed above.

V. PURITY OF SILICA AEROGEL

Silica aerogel can be made very pure and this is a major reason for its selection in the preparation of full density glass light guides in the glass industry. As mentioned earlier in this report, the process involves sol-gel (solution) chemistry, with subsequent supercritical extraction of the alcohol. The precursor materials, TMOS, water, and methanol, can all be obtained in high purity form or purified by fractional distillation before use. Thus, the gel that forms in the mold is relatively high purity silica, whose surfaces have hydroxyl groups for each non-siloxane bonded surface silicon atom. The solution

surrounding the solid consists mostly of methanol and some residual water.

After the extraction of the methanol, the residual organic content of the silica depends on the method used. For example, if the liquid methanol is first exchanged with another non-organic solvent (e.g. liquid carbon dioxide) and the new solvent is supercritically extracted, only trace organics remain in the dried aerogel. However, if the methanol is directly supercritically extracted, methyl groups tend to replace the hydrogen on the silica surface under the high temperature (> 250 C) and pressure (> 1200 psi) conditions needed for this method. This method is preferred when a material with a hydrophobic surface character is desired, whereas the former method yields a material with a hydrophilic character. We use either process at LLNL depending on the application for the aerogel.

Typically, aerogels of the hydrophobic type will have 1.1% by weight of hydrogen and 4% by weight of carbon. Some of the hydrogen content (~0.1%) is from water molecules adsorbed on the aerogel pore surfaces. However, aerogels of the hydrophilic type will typically have 0.4% by weight of hydrogen and less than 0.06% by weight of carbon. These values are obtained by combustion analysis of solid aerogel.

If desired, it is possible to reduce the organic content by heat treating the silica aerogel. We have done this to reduce the carbon content to trace amounts for some applications. However, the aerogel becomes very hydrophilic, absorbing water from the atmosphere after this process. Curves for the measured reduction of carbon and hydrogen as a function of temperature are shown in Fig. 7 for both cases of heating in air and heating in inert gas.

Inorganic impurities would most likely come from the high temperature autoclave processing. We have routinely analyzed the silica aerogels for such impurities and do not find metal impurities in our silica aerogels, with one exception. We have measured copper metal, at about 20 ppm impurity level, from aerogels that have been extracted from one of our autoclaves which has a copper D-ring seal. Also, although it has never been detected as an aerogel impurity, we have seen residue, containing molybdenum, on the surfaces of the aerogel. We believe that this residue is from the molybdenum-disulfide thread lubricant we use with two of our autoclaves.

The autoclave vessels we use are all made from 316 stainless

steel, that contains nominally 18% chromium, 11% nickel, and 2.5% molybdenum. One of the autoclaves uses a copper sealing ring, the others have stainless steel seals. The aerogels are usually cast in pyrex glass molds and the molds are supported within the autoclaves on stainless steel wire baskets. Other mold materials have been used (e.g. stainless steel, aluminum, and teflon) with varying degrees of success. Other sources of inorganic impurities would be in the solvents used, or would come from handling the material. However, a typical spectrochemical analysis of the low density aerogel, Fig. 8, shows no impurities above the minimum detectable levels.

VI. FACTORS FOR SUCCESSFUL AEROGEL EXTRACTION

It is difficult to obtain uncracked silica aerogels with specific sizes and shapes because of the many interacting factors that affect the process. We have made considerable progress to identify and control the most important factors leading to monolithic silica aerogels, but we have been less successful with specific sizes and shapes. These issues will be discussed briefly.

Cracking likely occurs in aerogels from the stresses it undergoes during the removal of the liquid within its ultra-fine pores. But we have found that other factors can contribute to or inhibit cracking by affecting the degree of stress (or stress gradients) within the gel. For example, the heat that is released as the gel forms from solution can drive convection flow that results in stress gradients in the material. We find this can be controlled by curing in a constant temperature bath and a mild anneal of the cured gel at 50 degrees centigrade. We have observed the ultra-low density gels to swell in the mold, as much as 20 volume percent, then shrink to about 10 percent less than original volume, during the high temperature supercritical extraction. This motion can grossly stress the aerogel if the part is not fully detached from the mold walls or if there is considerable friction at the gel/wall interface. Thus, we have found it necessary to use new, smooth surfaced glass molds to control this effect. We have also found that the swelling motion of the gel occurs during heat-up in the autoclave cycle and that a most likely time for cracks to occur is when the critical temperature is reached. Slowing the heating rate to less than 0.3 degrees centigrade per minute through the critical temperature (242 C for methanol) has been sufficient to limit

cracking to less than 10% of our samples. In Fig. 9, we show a typical temperature and pressure vs. time profile for the autoclave extraction that we have found successful.

It is, of course, desirable to have homogeneous and uniformly sized silica aerogel parts for the particle capture application. The ultra-fine microstructure of aerogel gives it inherently high homogeneity but its uniformity is affected by the drying process. The shrinking of the gel is not uniform during the extraction, and this leads to distorted shapes. In particular, the shrinkage is highest near the open end or ends of the mold, indicating that the shrinkage is sensitive to the rate of vapor extraction from the gel pores. However, our measurements show that the effect is independent of the rate of decompression of the methanol vapor. We are continuing to address this problem, currently emphasizing the temperature gradient within the autoclave as a possible factor.

VII. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

We have extended the density range from 0.1 gm/cc to 0.04 gm/cc to routinely make clear silica aerogels. Aerogels at densities less than 0.04 gm/cc have also been made but they have two problems: transparency is lost, and they are very weak. The first of these problems is probably due to the pore size becoming large enough, at ultra-low densities, to scatter light more efficiently. While it may be possible to control the formation of the microstructure in such a way as to reduce the density at which this occurs, a fundamental density limit ultimately exists. Below the density limit, it would be impossible to distribute the mass of the silica without having pores large enough to efficiently scatter light, thus producing an opaque material. We have estimated from a simple close-packed sphere model that the density limit would be about 0.015 gm/cc. The second problem, the weakness as density decreases, is expected for all polymeric materials but is especially dramatic in the aerogels. Our measurements show (Fig. 10) that the modulus of the silica aerogel changes as nearly the fourth power of the density, so that the aerogels at densities less than 0.02 gm/cc have very little strength. Again, while some gain in strength could result from controlling the formation of the microstructure, the combination of the two effects

mentioned here suggests that we are near a limit in usable material at 0.02 gm/cc.

An area that would definitely benefit from additional work is the shape distortion of the aerogel during extraction. We plan to use statistical exprimental design to determine through experimentation, the factors contributing to this effect, then move to solve this problem.

We believe that the silica aerogel can certainly be made ultra-pure (i.e. all impurities less than 10 ppm) with the proper attention given to this during processing. Two areas for improving the purity of our material would be: 1) special handling procedures at all steps of the process, and 2) higher purity precursor materials. We have shown that the organic content within the aerogel can be controlled at the expense of the stability of this material to humidity changes.

REFERENCES:

1. G. C. Ruben and M. W. Shafer (1986) "Stereo-TEM Imaging of Sol Gel Glass Surfaces," in Better Ceramics Through Chemistry II, C. J. Brinker, D. E. Clark and D. R. Ulrich, eds., Materials Research Society, Pitts. PA. Vol.73, pp 207-212.

2. R. K. Ile, The Chemistry of Silica, N.Y., Wiley Interscience, (1979), Chap. 3.

3. D. W. Schaefer, Science 243, 1023 (1989).

FIGURE TITLES:

Fig. 1   Absorbance of a typical silica aerogel from 200 to 800 nm.

Fig. 2   Photograph of two aerogel samples with different optical quality..

Fig. 3   Optical transmittance for the two samples in Fig. 2.

Fig. 4   Transmission Electron Micrographs (TEM) of the two samples shown in Fig. 2.

Fig. 5   Photograph of 20 aerogel samples made with various catalyst concentrations.

Fig. 6   Plot of the relative absorbance by the samples from Fig. 5 vs. catalyst concentration.

Fig. 7   Curves for the reduction of carbon and hydrogen in silica aerogel as a function of temperature.

Fig. 8   Spectrochemical analysis report for the silica aerogel.

Fig. 9   Typical temperature and pressure vs. time profile for an autoclave extraction.

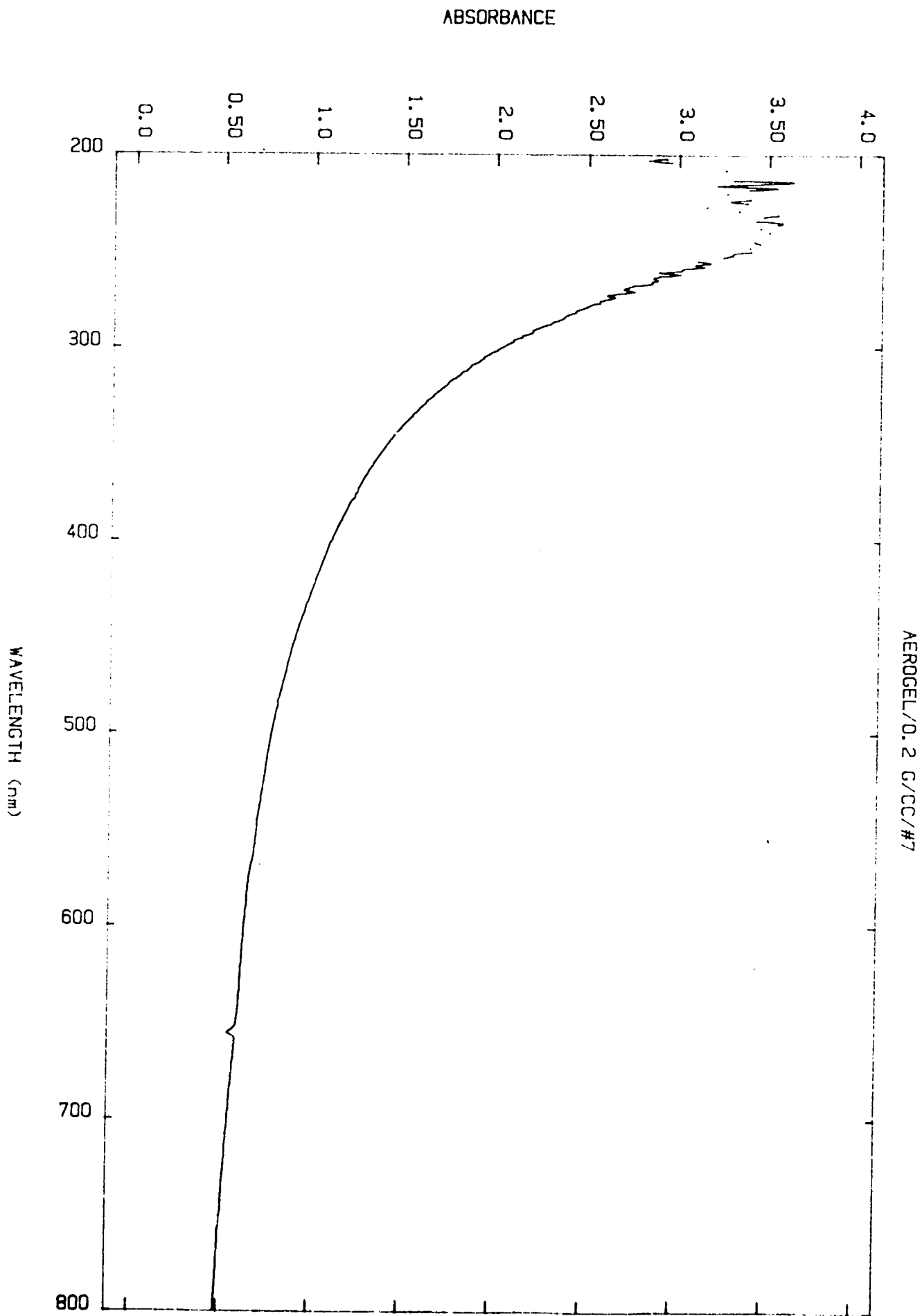Fig. 10   Modulus vs. density for two types of silica aerogels.

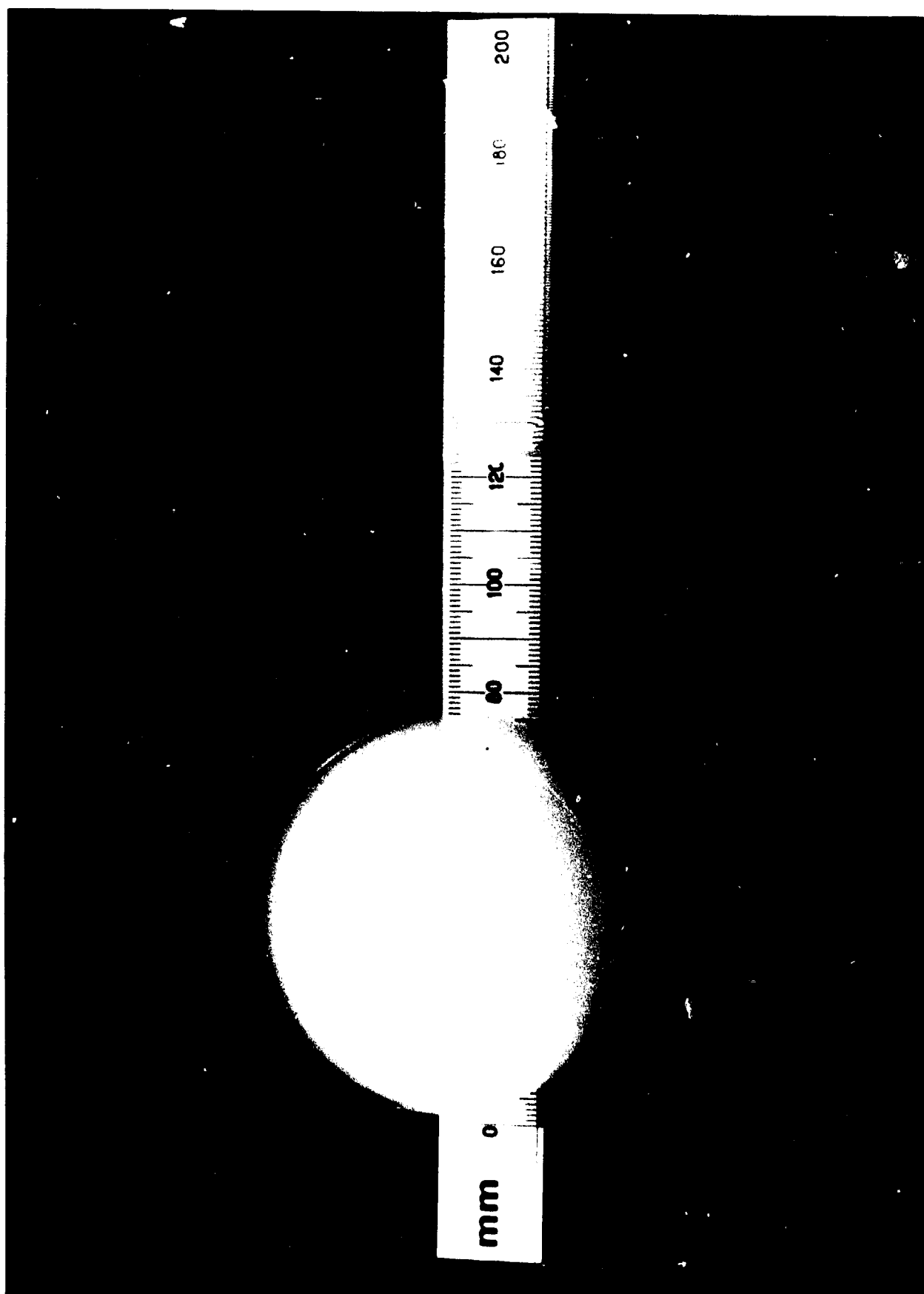**Fig. 1** **Absorbance of a typical silica aerogel from 200 to 800 nm.**

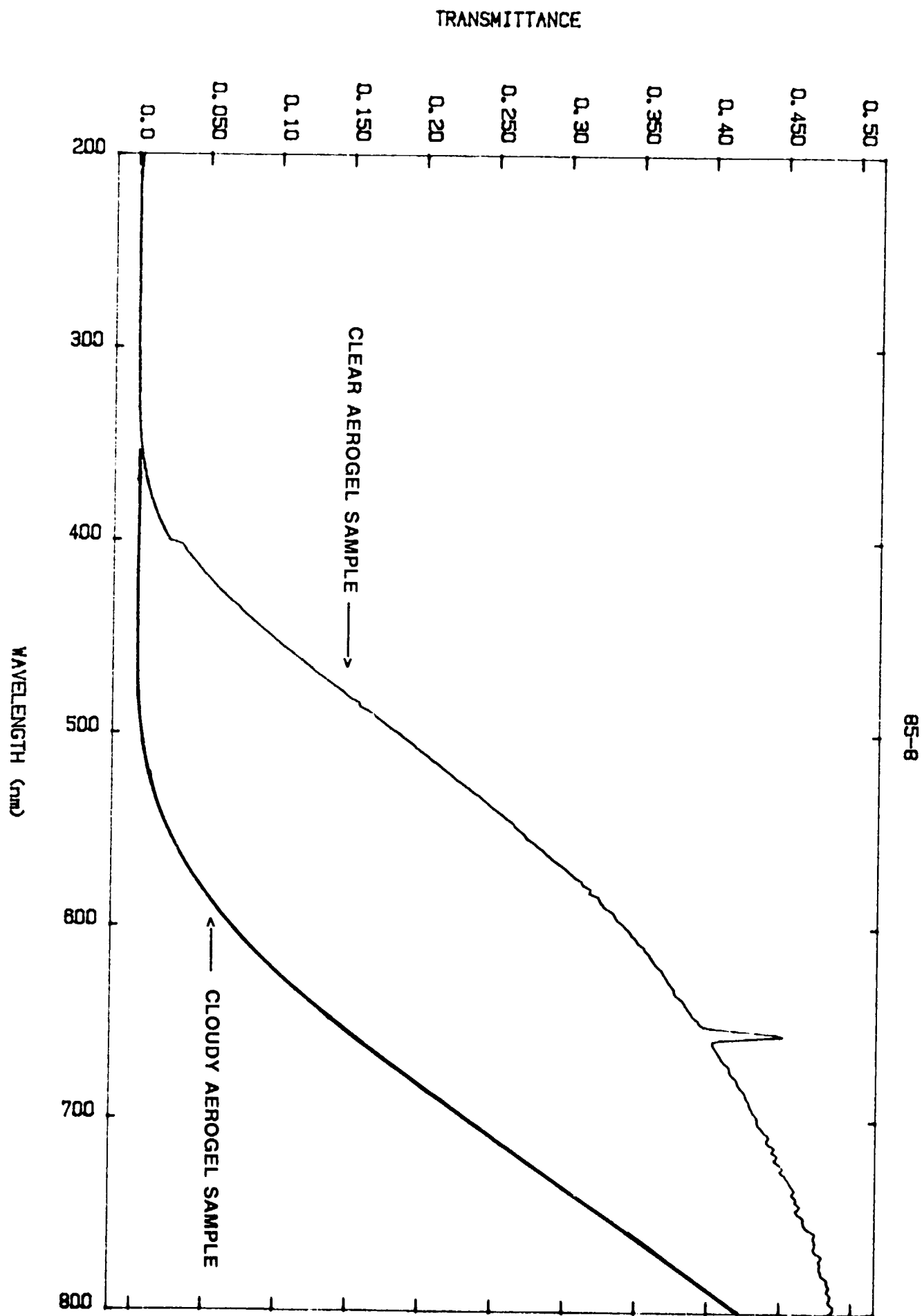**Fig. 2   Photograph of two aerogel samples with different optical quality.**

Fig. 3 Optical transmittance for the two samples in Fig. 2.

TEM of clear sample

TEM of cloudy sample

|----|
200Å

Fig. 4   Transmission Electron Micrographs (TEM) of the two
samples in Fig. 2.

Fig. 5 Photograph of 20 aerogel samples made with various catalyst concentrations.
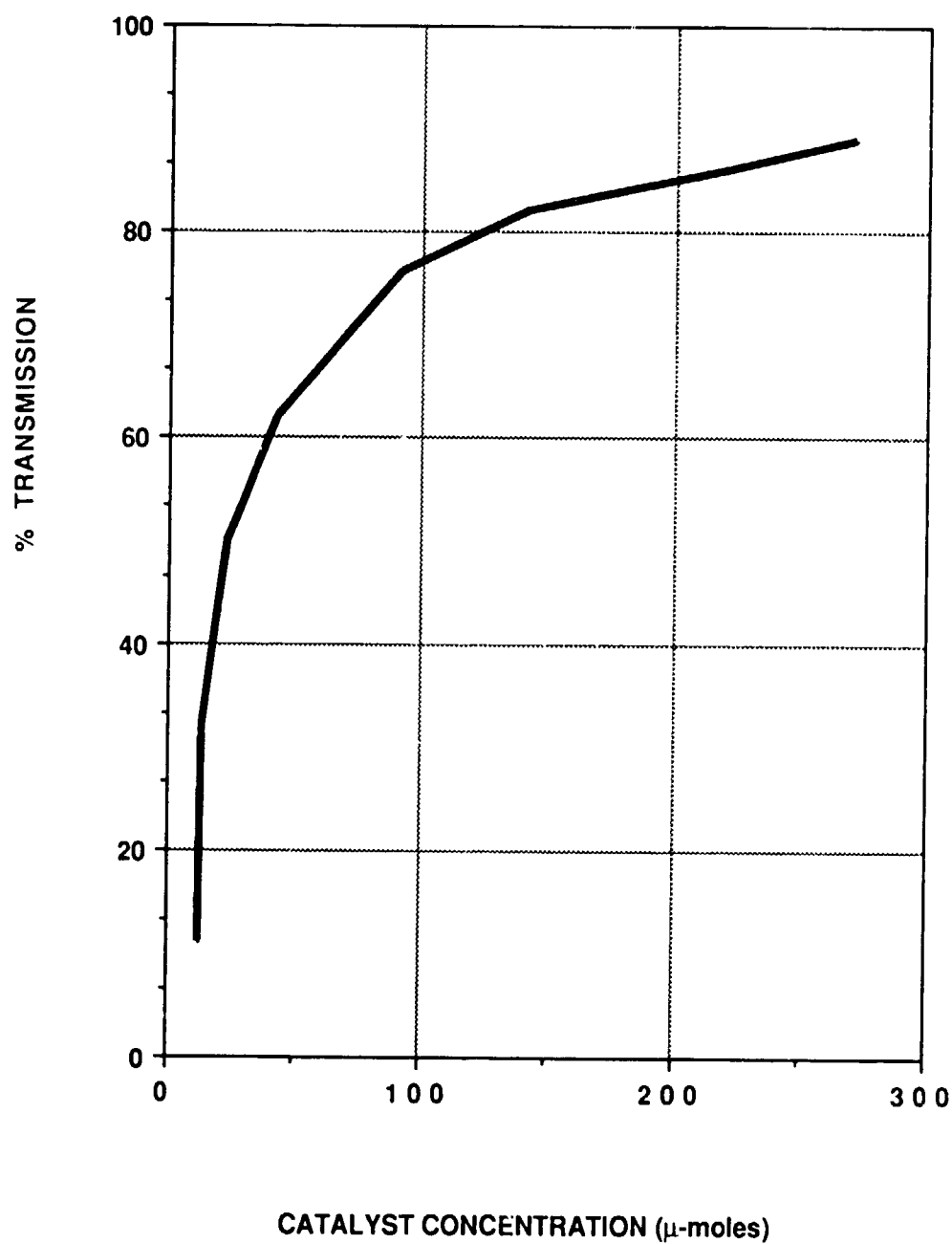
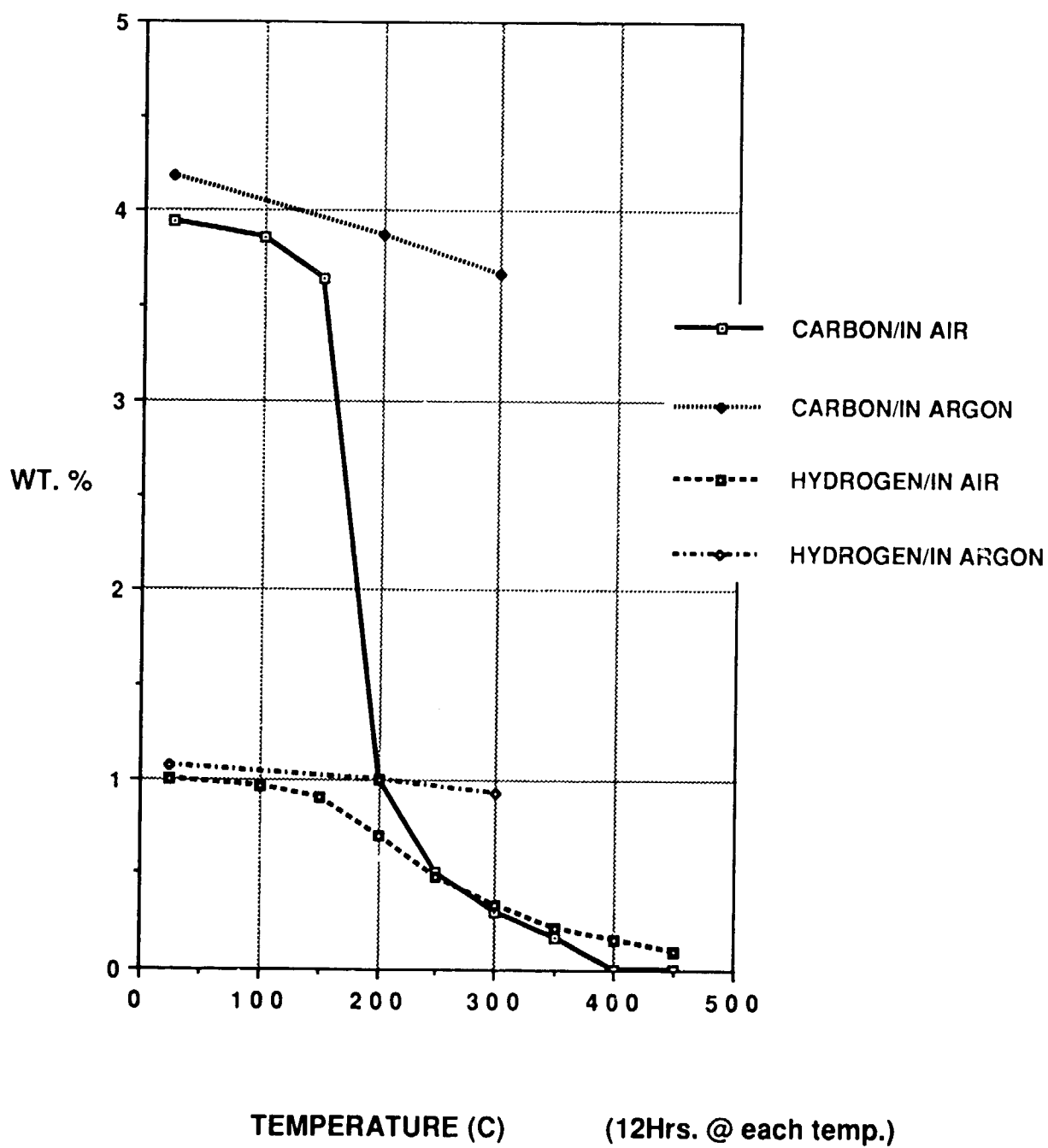**Fig. 6 Transmittance of the samples in Fig. 5 vs. catalyst concentration.**

Fig. 7 Carbon and hydrogen in silica aerogel vs. temperature.

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Sample No: ES890315   Received: 05/03/89   Plate No: 5142
Requester: J. Fischer   Reported: 05/08/89   5143
  Analyst: B. Armstrong
Signature: Disk No: 55

Sample Description: Aerogel, JPO127-A

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Note: This SEMIQUANTITATIVE ANALYSIS is based on a comparison of the
      sample with closely matched matrix standards. For elements "Not
      Detected", the number cited is the concentration required to confirm
      its presence. The reported values are typically within +/- 50% of
      the true value. If more accurate quantitative determinations are
      needed, a request should be made specifying the elements of interest
      and the accuracy needed.
      The elements reported below were the only ones sought.*

==
* The results shown are listed by amount found.

Element	Not Detected	Found (ppm) by weight	Element	Not Detected	Found (ppm) by weight
Ir	<1000		Hg	< 30	
W	< 300		La	< 30	
Ta	< 300		Sn	< 30	
P	< 300		Fe	< 10	
U	< 300		Zr	< 10	
Hf	< 300		Lu	< 10	
Cd	< 100		Ca	< 10	
Dy	< 100		V	< 10	
Tb	< 100		K	< 10	
Th	< 100		Rh	< 10	
Sm	< 100		Ge	< 10	
Tl	< 100		Tm	< 10	
Nd	< 100		Ba	< 3	
Re	< 100		Ga	< 3	
Pr	< 100		Co	< 3	
Pb	< 100		Al	< 3	
As	< 100		Pd	< 3	
Pt	< 100		Sc	< 3	
In	< 100		Eu	< 3	
Sb	< 30		Na	< 3	
Mo	< 30		Ti	< 3	
Ru	< 30		Ni	< 3	
Bi	< 30		Cu	< 3	
Er	< 30		Au	< 3	
Rb	< 30		Mn	< 1	
Ho	< 30		Mg	< 1	
Y	< 30		B	< 1	
Cr	< 30		Ag	< 1	
Nb	< 30		Li	< 1	
Gd	< 30		Sr	< 1	
Zn	< 30		Be	< 1	
Ce	< 30				
Yb	< 30				

Fig. 8   Spectrochemical analysis report for the silica aerogel.

TEMPERATURE (C)

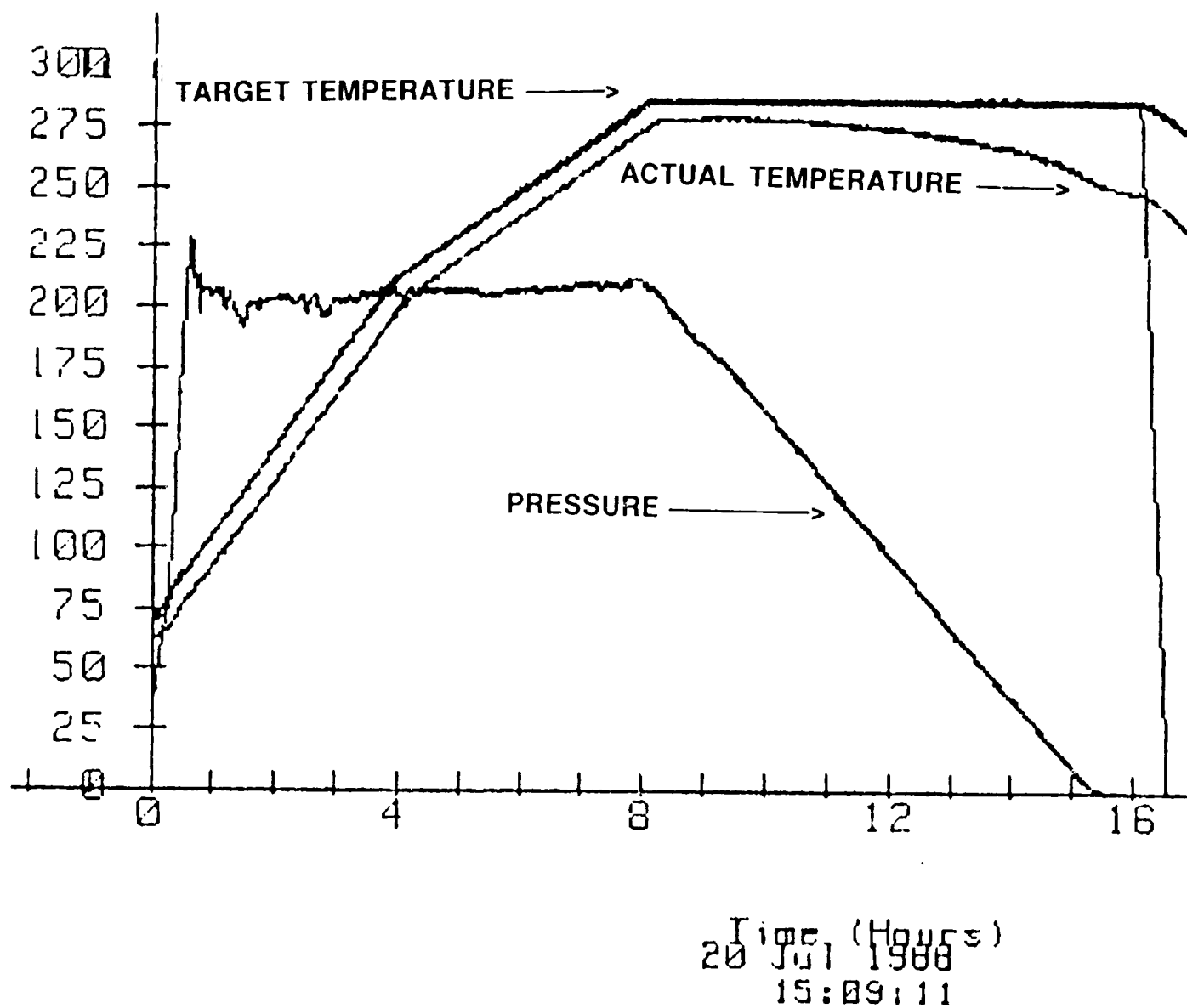PRESSURE (X10, PSI)

Fig. 9   Temperature and pressure vs. time for a typical
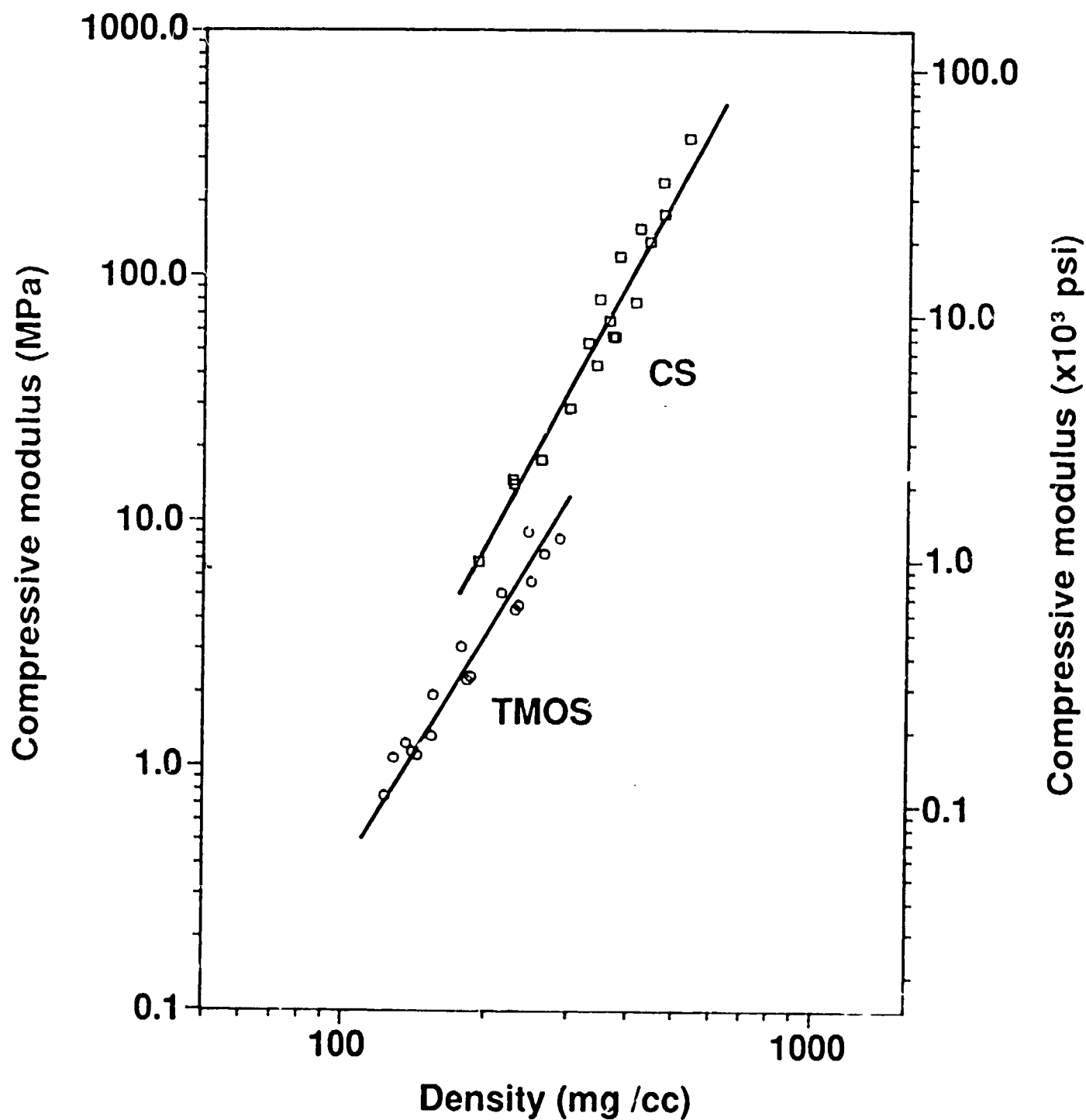   autoclave extraction run.

Fig. 10   Modulus vs. density for two types of silica aerogels.